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PERFORMANCE-ENHANCING MATERIALS FOR FUTURE GENERATION EXPLOSIVES AND PROPELLANTS

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14. ABSTRACT

During this grant, SRI has made progress in areas of interest to Navy work thrusts, specifically ammonium perchlorate oxidizer replacement and candidates for insensitive munitions. N-oxidation of nitro-heterocycles can boost oxygen content and increase density of the parent material. Through this work, synthesis methodology for more difficult ring N-oxidation of a variety of nitroheterocycles has been expanded. SRI has explored the limits of N-oxidation using hypofluorous acid (HOF) and persulfate (OXONE) of a variety of nitro substituted 1,2,4-triazoles, 1,2,3-traizoles and imidazoles. SRI also explored the synthesis of a variety of 5/6/5 and 5/5 fused heterocycle ring systems. SRI also explored the synthesis and properties of over-oxidized trinitromethyl ($Cring-C(NO_2)_3$) substituted heterocycles. Several examples of 1,2,4-triazole and bi-1,2,4-triazoles with trinitromethyl substitution were synthesized and characterized. This grant has generated several compounds that hold promise as candidates for replacement of ammonium propellant formulations, and/or insensitive munitions and require further investigation.

15. SUBJECT TERMS
High Energy Density Oxidizers, Insensitive Munitions, N-Oxidation, High Nitrogen Heterocycles, Trinitromethyl, Fused Heterocycles

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Performance-Enhancing Materials for Future Generation Explosives and Propellants

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Introduction

SRI International's (SRI) participation in the current Office of Naval Research (ONR) Energetic Materials Program began late in 2008. Our first-year effort was to generally synthesize candidate targets for high-performing insensitive energetic materials. During this initial period, SRI improved the larger-scale synthesis of ammonium 2-oxy-5-nitrotetrazole (AONT, SRI, 2003), which resulted in the synthesis of 25 grams of AONT for further testing. This compound holds promise as a Navy minimum-smoke propellant ingredient. During this period, SRI also explored the synthesis of a variety of 5/6/5 and 5/5 fused heterocycle ring systems. This work resulted in the discovery of 1,1'-diamino-4,4',5,5'-tetranitro-2,2'-biimidazole, a highly dense, thermally stable, and energetic material. SRI also undertook efforts to prepare the corresponding azo-linked 5/6/5 structure. The emphasis of our work narrowed in the second and third years to alternative high-energy and dense oxidizers (HEDO) to replace ammonium perchlorate (AP). Requirements for a new oxidizer include a density of ~ 2.0 g/cc, oxygen content greater than AP, m.p. > 150°C, sensitivity no worse than that of PETN, low hydrogen and carbon (high nitrogen and oxygen), and ability to be synthesized from inexpensive bulk materials. In response, SRI initiated an exploration of methods to increase the oxygen content of nitro-heterocycles by ring N-oxidation. Current methods using peracids and persulfates do not have the oxidizing power to oxidize relatively unreactive nitroheterocycles. SRI has explored the use of hypofluorous acid (HOF) to oxidize a variety of nitrogenous rings. Through this work, SRI has discovered that HOF oxidation of 3,5-dinitro-1,2,4-triazole is very fast and efficient. This has enabled the discovery and potential utility of a new family of energetic salts of the 1-oxy-3,5-dinitro-1,2,4-triazole anion. The ammonium and potassium salts were synthesized and characterized and may find use as Navy minimum-smoke propellant ingredients. SRI has also explored the synthesis of the 4,5-dinitro-1,2,3-triazole ring and N-oxides as candidate oxidizer ingredients. This work resulted in a convenient synthesis for a series of 1-alkyl-4,5-diamino-1,2,3-triazole starting materials. Under diazotizing conditions with excess nitrite, the 1-t-butyl-4,5-diamino-1,2,3-triazole gives the interesting 5/5 fused-ring, triazolotriazole. This system represents a starting point for potentially high-performance, fused-ring systems. The N2-oxidation of potassium 4,5-dinitro-1,2,3-triazole by persulfate (OXONE) has given dense over-oxidized salts of 2-oxy-4,5-dinitro-1,2,3-triazolate with high thermal stability. This class of compounds holds promise as both candidates for ammonium perchlorate replacement and as insensitive munitions and requires further investigation. SRI has also synthesized examples of C_{ring} trinitromethyl-substituted energetic nitrogenous heterocycle structures. Three examples of 1,2,4-triazole and bi-1,2,4-triazoles with trinitromethyl substitution on a ring carbon were synthesized and characterized. They are easily prepared, expectedly very dense, and have a high oxygen balance with a range of thermal stabilities.

Results and Discussion

The discussion below summarizes SRI's accomplishments in the Energetic Materials Program under the direction of Dr. Cliff Bedford of ONR since September 2008. Our discussion below emphasizes compounds that may find actual practical value and/or are key intermediates to future targets of interest to the Navy.

Fused-Ring Heterocycle Systems

State-of-the-art explosives research has taken the approach of maximizing density by the construction of condensed polycyclic caged molecules. The strain of the cage contributes to the heat of formation, and the compact nature of the cage increases density. This vein of work, led primarily by ONR researchers in the last 15 years, has produced explosives such as Cl-20 (hexanitrohexaazaisowurzitane) (ρ = 2.04 g/cc) and octanitrocubane (ρ = 1.979 g/cc). However, a key disadvantage of these explosives has been their relative difficulty of synthesis. Comparatively little work has been done on the more easily synthesized fused multicyclic (3 or more rings) heterocyclic explosives. Examples of these are TACOT (tetranitro-2,3,5,6-dibenzo-1,3a,4,6a tetrazapentalene) (ρ = 1.82 g/cc) and the dinitropyridine-based TACOT analogues (ρ = 1.88 g/cc). Portions of these molecules, however, are largely carbocyclic. Since nitrogenous heterocycles are substantially denser than their carbocyclic analogs, our approach has been the fusion of "high-nitrogen" heterocycles to give a planar molecular array that maximizes density.

During this program, SRI targeted the azo (**1**) and dinitroethylene (**2**) bridged 4,4',5,5'-tetranitro-2,2'-biimidazole fused-ring systems shown below.

1, ($C_6N_{10}O_8$)   **2**, ($C_8N_{10}O_{12}$)
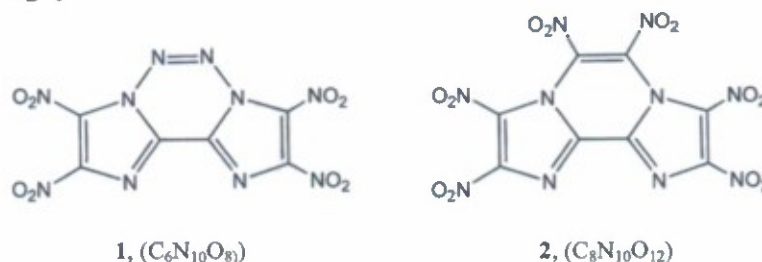
We prepared 4,4',5,5'-tetranitro-2,2'-bi-1H-imidazole as shown in Scheme 1 by the nitration of 2,2'-bi-1H-imidazole with 100% fuming nitric acid in 100% sulfuric acid according to the procedure of Cho et al.[1] Purification of this material was facilitated by preparation and crystallization of the dipotassium salt, followed by protonation with sulfuric acid and crystallization. Amination of the 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) salt with hydroxylamine-O-toluene sulfonate gave 1,1'-diamino-4,4',5,5'-tetranitro-2,2'-biimidazole, **3**. Approximately, 1 gram of **3** has been prepared to date. Compound **3** has a crystal density of 1.937 g/cc (21°C) by X-ray. The X-ray structure shown in Figure 1 shows that the two imidazole rings are coplanar; calculated hydrogen bonding distances suggest pyramidal N-NH$_2$ groups that are in the plane of the biimidazole rings, with nitro groups settling slightly rotated out of this plane. The differential scanning calorimetry (DSC) shows that **3** is stable up to ~ 200°C (Figure 2).
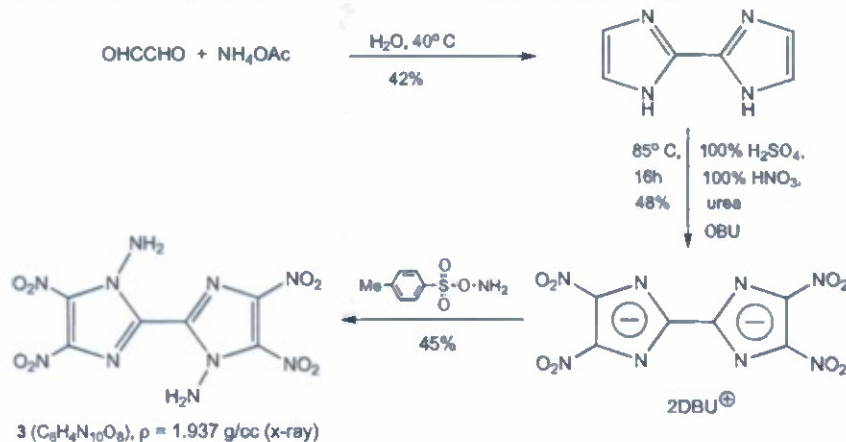
Scheme 1. Three-step synthesis of 1,1'-diamino-4,4',5,5'-tetranitro-2,2'-biimidazole, **3**.

(A)

(B)

Figure 1. Overhead (A) and side (B) ORTEP views of 1,1'-diamino-4,4',5,5'-tetranitro-2,2'-biimidazole, **3**.

Figure 2. DSC of 1,1'-diamino-4,4',5,5'-tetranitro-2,2'-biimidazole, **3**.

Unfortunately, recent tests have revealed that DATNBI is unstable to hydrolysis in aqueous methanol. Oxidative coupling of the N-amino functional groups to give **1** was attempted as shown in Scheme 2. Oxidants such as t-BuOX (X = Cl, Br), $PhSeO_2H$ and HgO gave limited success in driving this transformation. A compound with a consistent nuclear magnetic resonance (NMR) and infrared (IR) spectrum for **1** was obtained in low yield by using t-BuOCl. Reaction with dichloroisocyanurate in acetonitrile/water gave higher yields of the proposed compound **1**. We have not been able to unambiguously define the structure since growing crystals of **1** for X-ray analysis has been problematic.

Scheme 2. Oxidative diamino coupling reaction of **3**.

Various pathways to dinitroethylene-bridged **2** have been attempted. Reaction of the DBU salt of 4,4',5,5'-tetranitro-2,2'-biimidazole with dichloroglyoxime gave an intractable mixture of products on workup. Reaction with cyanogen dioxide (ONC-CNO) prepared *in situ* also gave a mixture of products (Scbeme 3).


2, $C_6N_{10}O_{12}$

Scheme 3. Attempts at synthesis of dinitroethylene-bridged 5/6/5 ring systems.

SRI pursued other fused 5/5 ring precursors during this program that in theory can be nitrated and ring-N-oxidized to give bighly oxidized and dense compounds. We prepared 1-bydroxy-5-aminotetrazole (HAT) by reacting O-benzylhydroxylamine with cyanogen bromide followed by cyclization with triethylammonium azide and then debenzylation according to a procedure developed in our lab. Attempts have been made to insert a formyl group between tbe pendant amino and hydroxyl groups of 1-bydroxy-5-aminotetrazole as sbown in Scbeme 4 using triethyl orthoformate and zirconium oxychloride[2] or sulfamic acid[3] catalysts in alcohol and with heat.
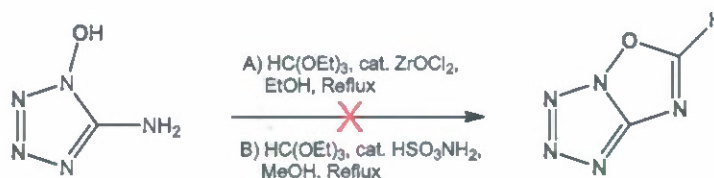
Scheme 4. Attempted cyclization of HAT by formylation.

Attempts have heen made to insert a formyl group hetween the two amino groups of 1,5-diamino-3-nitro-1,2,4-triazole (AANTA) as shown in Scheme 5 using either formic acid and heat or triethyl- or trimethyl-orthoformate and zirconium oxychloride or sulfamic acid catalysts in alcohol with heat. An intermediate imine adduct characterized hy x-ray crystallography was obtained as shown in Scheme 5.
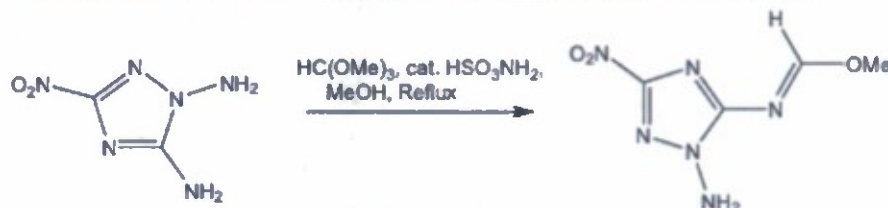
Scheme 5. Attempted cyclization of AANTA by formylation.

Attempts to react AANTA with 1,1-diiodo-2,2-dinitroethylene (prepared hy the controlled nitration of tetraiodoethylene with 90% nitric acid) as shown in Scheme 6 were unsuccessful.[4] In contrast, the known reaction hetween 1,1-diiodo-2,2-dinitroethylene and 1,2-phenylenediamine proceeded smoothly.


Scheme 6. Bi-heterocycles from 1,1-diiodo-2,2-dinitroethylene.

Novel Oxidizing Anions

Ammonium 2-Oxy-5-Nitrotetrazole. In 2008, ONR expressed interest in the larger-scale synthesis of ammonium 2-oxy-5-nitrotetrazole (AONT), 4, which was first discovered at SRI in 2003 under funding provided hy the DARPA high-nitrogen project and was the suhject of a scale-up Phase-I Small Business Innovation Research (SBIR) effort funded hy the Air Force Office of Scientific Research (AFOSR).[5] The compound has a density of 1.703 g/cc at 20°C and an estimated heat formation of ~ 40 kcal/mole. This compound is a promising new energetic material that may find use as a propellant ingredient for minimum-smoke applications. Propellant manufacturers have expressed an interest in this compound for scale-up. During 2008, SRI synthesized 25 grams of this material for safety and small propellant hand mixes for evaluation hy ONR, China Lake. During this scale-up exercise, the yield of the $(n\text{-Bu})_3NH^+$ salt to the NH_4^+ salt conversion was increased from 60% to 90% using a different solvent system. The purity of the N2-oxide was verified hy ion chromatography to be > 99.5% (< 0.5% ANT). The improved large-scale procedure for the synthesis of AONT was thoroughly documented in a standard operating procedure (SOP) and sent to ONR (Scheme 7).
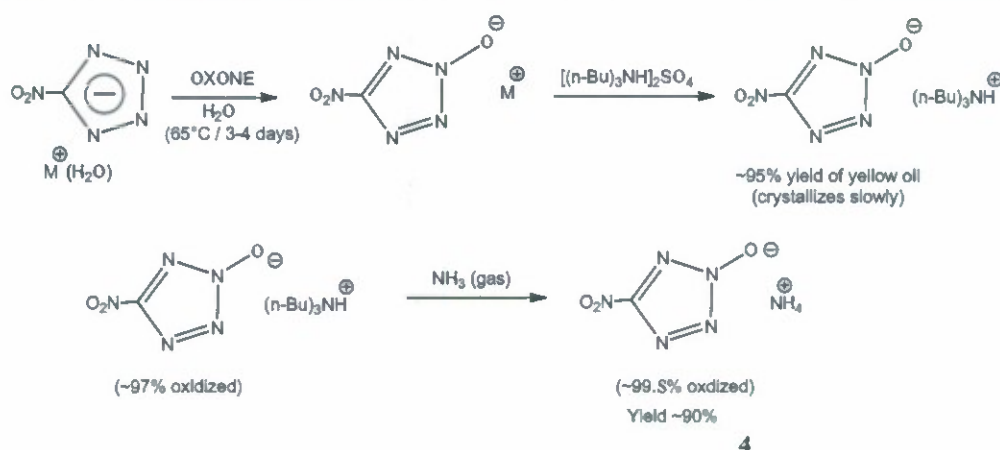
Scheme 7. Large-scale synthesis for ammonium 2-oxy-5-nitrotetrazole (AONT), 4.

Ammonium 1-Oxy-3,5-Dinitrotetrazole. ONR has also expressed interest in the over-oxidized 1-oxy-3,5-dinitro-1,2,4-triazole anion. Salts of the anion were projected to have higher density than those of the 2-oxy-5-nitrotetrazole and higher oxygen content. The 1-oxy-3,5-dinitro-1,2,4-triazole anion was first prepared at SRI during an Integrated High Payoff Rocket Propulsion Technology (IHPRPT) project as part of a search for liquid oxidizers.[6] At that time, the 3,5-dinitro-1,2,4-triazole (DNT) was oxidized using peroxysulfate (OXONE), followed by methylation and the liquid 1-methoxy-3,5-dinitro-1,2,4-triazole separated from the 1-methyl-3,5,-1,2,4-triazole impurity. Oxidation of DNT by OXONE was slow and inefficient, and pure salts of 1-oxy-3,5-dinitro-1,2,4-triazole were not isolated. During this ONR program, we have explored the use of alternative oxidants such as hypofluorous acid (HOF) to oxidize a variety of nitrogenous rings. SRI has discovered that HOF oxidation in the case of 3,5-dinitro-1,2,4-triazole is very fast (within 15 minutes at -5°C compared to OXONE, 4-5 days at 55°C, < 25%) giving ~65% yield of potassium 1-oxy-3,5-dinitro-1,2,4-triazole (KODNT), **5** of 98.5% purity after re-crystallization (Scheme 8). The ammonium salt was prepared for the first time during this program and characterized by ion chromatography, IR, DSC, and X-ray crystallography. Ammonium 1-oxy-3,5-dinitro-1,2,4-triazole (AODNT), **6** salt has a respectable crystal density of 1.784 g/cc at ~ 23°C (1.81 g/cc for ADN) and an estimated ΔH_f = +25 kcal/mole (see Figure 3 for ORTEP drawing). The density of AODNT is ~ 0.15 g/cc greater than the ammonium salt (ADNT) of the parent. AODNT does not melt by DSC but gives a very sharp exothermic event with onset to decomposition at 145°C (Figure 4). The potassium salt has a crystal density of 2.08 g/cc and a melting point of 215°C with decomposition.
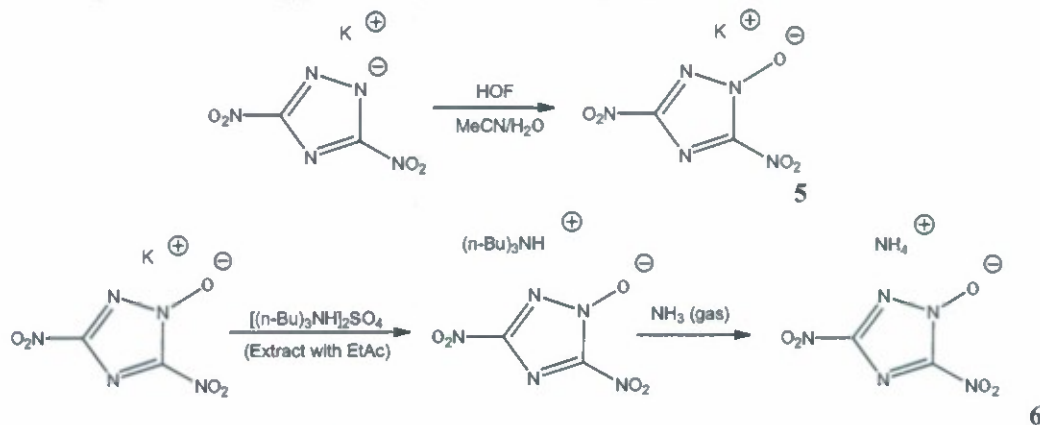
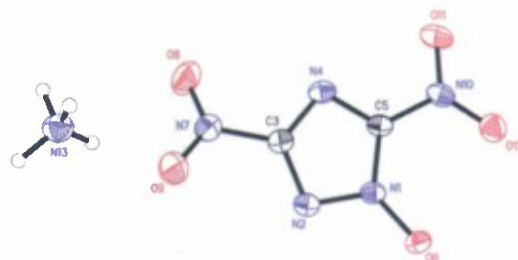**Scheme 8.** Synthesis of ammonium 1-oxy-3,5-dinitro-1,2,4-triazole (AODNT), **6.**

Figure 3. ORTEP drawing for the structure of AODNT, **6**.
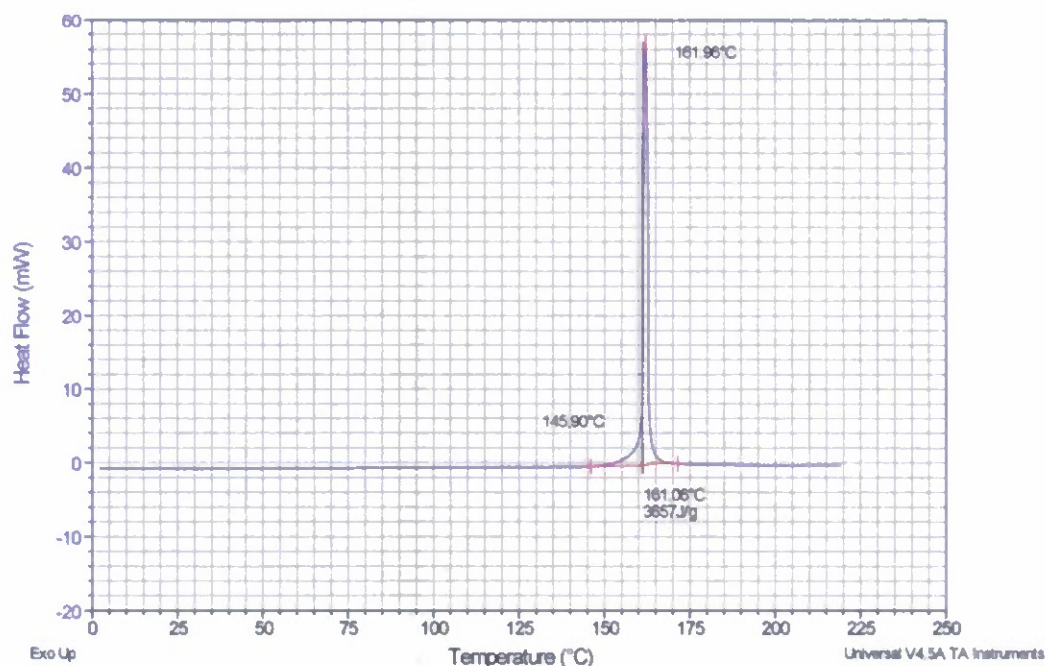
DSC of Ammonium 3,5-Dinitro-1-Oxytriazole

Figure 4. DSC of AODNT, **6**.

Ammonium 2-Oxy-4,5-Dinitro,1,2,3-Triazole. As a natural extension of our work on the elaboration of 5-nitrotetrazole and 3,5-dinitro-1,2,4-triazole by ring oxidation and amination, we are pursuing 4,5-dinitro-1,2,3-triazole as an energetic framework. The 1,2,3-triazole is predicted to provide higher density and heat of formation compared to the 1,2,4-triazole system. While pursuing the synthesis of 4,5-dinitro-1,2,3-triazole, we found the route established by Baryshnikov et al. to be lengthy and involving the *in situ* generation of hydrazoic acid.[7] We have developed a 3-step synthesis of 1-R-4,5-diamino-1,2,3-triazole (R = t-Bu, benzyl, *p*-methoxybenzyl (PMB) and CPh₃) (shown in Scheme 9). The structure of 1-t-butyl-4,5-diamino-1,2,3-triazole was confirmed by X-ray crystallography. We have attempted to convert this product into 4,5-dinitro-1,2,3-triazole by Sandmeyer reaction or single-step oxidation reactions.
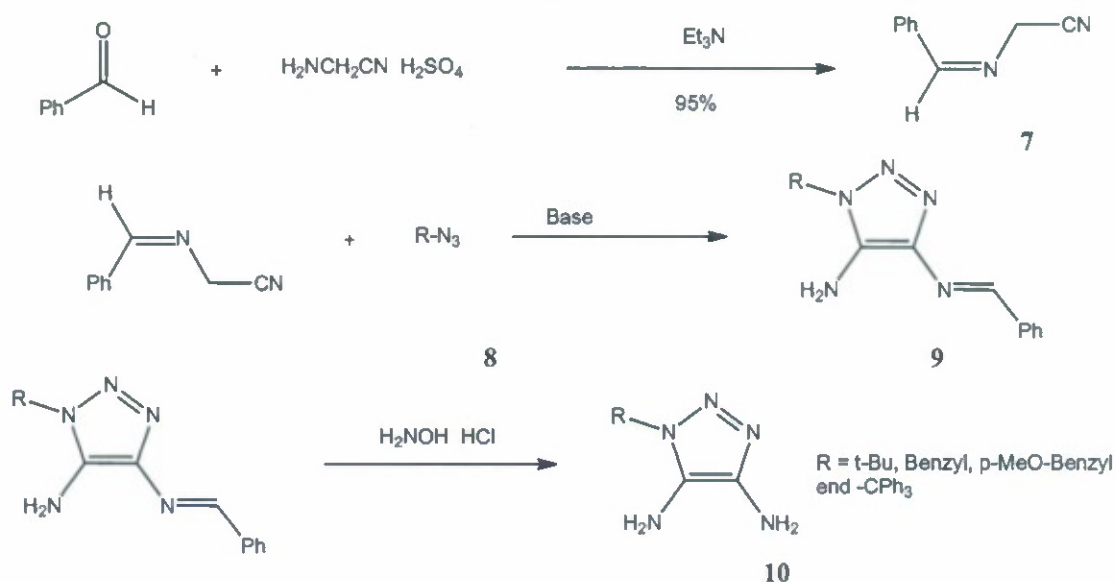
Scheme 9. General synthesis of 1-alkyl-4,5-diamino-1,2,3-triazoles.

Using diazotization conditions with excess nitrite gave the interesting 5/5 fused-ring, triazolotriazole in 75% yield (see Scheme 10). The structure of the triazolotriazole was confirmed by X-ray crystallography. The 5/5 rings sit on a mirror plane. This molecule has potential as a precursor to other interesting 5/5 fused-ring energetic materials and synthetic methodology could give other 5/5 fused-ring systems.
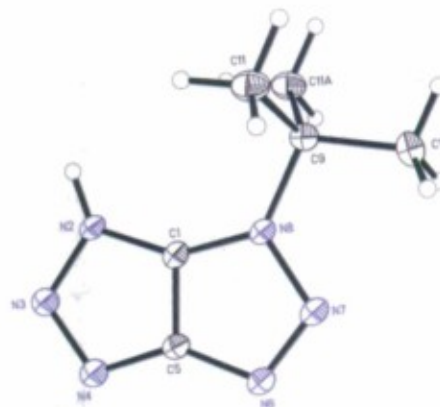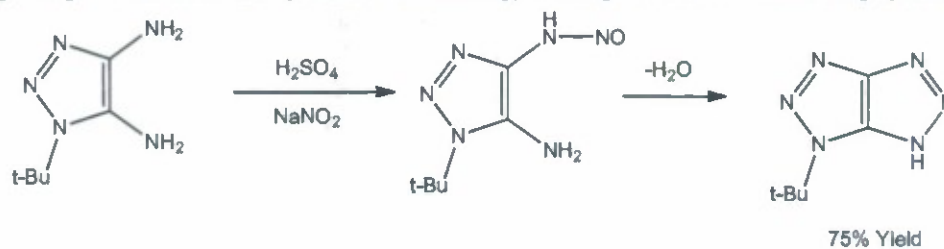
Scheme 10. Diazotization resulting in 1-t-butyl-triazolotriazole.

We have attempted single-step direct oxidation of 1-t-butyl-4,5-diamino-1,2,3-triazole by the peroxide/sulfuric acid and peroxide/sodium tungstate systems reportedly used to oxidize 4,5-diaminofurazan to 4,5-dinitrofurazan. The reactions only gave mixtures of intractable decomposition products. The oxidation of 1-t-butyl-4,5-diamino-1,2,3-triazole by excess HOF in acetonitrile/water was partially successful. Reaction after ~ 30 min. at -5°C gave ~ 35% isolable yield of 1-t-butyl-4,5-dinitro-1,2,3-triazole. The structure was confirmed by X-ray crystallography (Figure 5).
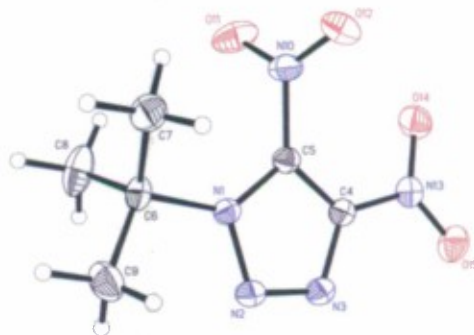

Figure 5. ORTEP drawing for the structure of 1-t-butyl-4,5-dinitro-1,2,3-triazole.

Attempts to deprotect either 1-t-butyl-4,5-diamino-1,2,3-triazole or 1-t-butyl-4,5-dinitro-1,2,3-triazole in refluxing trifluoroacetic acid (TFAA) returned starting materials. Oxidation of 1-*p*-metboxybenzyl-4,5-diamino-1,2,3-triazole using HOF gave mixtures of 1-*p*-methoxybenzyl-4-nitro-5-amino-1,2,3-triazole, **11** and 1-*p*-metboxybenzyl-4,5-dinitro-1,2,3-triazole, **12**. The reaction was observed to give an initial blue color that extinguishes after a very sbort time (< 30 sec.). The blue color is attributed to a C-nitroso intermediate oxidation product. It was discovered that quencbing the reaction by addition of saturated aqueous bicarbonate solution immediately after the blue color extinguisbes gave a good isolable yield (72%) of the 1-*p*-methoxybenzyl-4-nitro-5-amino-1,2,3-triazole, **11** assumed isomer (Scbeme 11). Only one isomer is observed in the ¹H-NMR spectrum. The *p*-methoxybenzyl (PMB) group from **11** and **12** is easily removed by refluxing in TFAA for ~ 36 hrs to give high yields of 4-amino-5-nitro-1,2,3-triazole, **13** (85%) and 4,5-dinitro-1,2,3-triazole, **14** (99%).
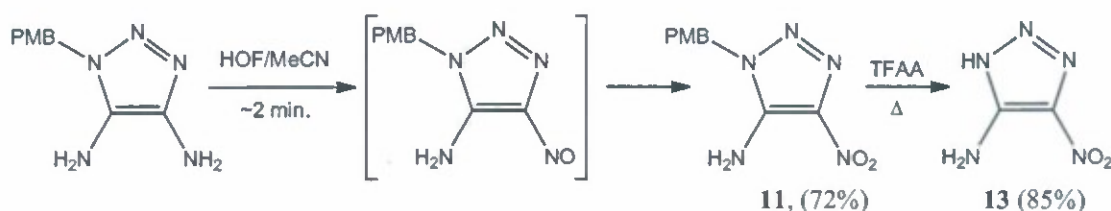
Scheme 11. Hypofluorous oxidation and deprotection of 1-*p*-methoxybenzyl-4,5-diamino-1,2,3-triazole.

The 4-amino-5-nitro-1,2,3-triazole can be oxidized by H_2O_2/H_2SO_4 to 4,5-dinitro-1,2,3-triazole following a procedure reported by Baryshnikov et al.[7] An amount of potassium 4,5-dinitro-1,2,3-triazole was synthesized using both the SRI and Baryshnikov routes to attempt the N-oxidation of the 1,2,3-triazole ring. Near the end of this grant, it was discovered tbe 4,5-dinitro-1,2,3-triazole system is easily N-oxidized by buffered aqueous OXONE using a procedure previously developed at SRI for the N-oxidation of 5-nitrotetrazole. After approximately 48 hrs at ~ 55°C, the solution was acidified and the oxy-4,5-dinitro-1,2,3-triazole free acid extracted using diethyl ether. The acid is easily converted to the potassium

or ammonium salt using potassium carbonate and ammonia, respectively. Preliminary analysis of the potassium salt by ion chromatograpby clearly sbows greater than 96% conversion to the oxy-4,5-dinitro-1,2,3-triazole target. This extent of N-oxidation via OXONE is similar to that of 5-nitrotetrazole and contrasts with the lower conversion (~60%) observed for the 3,5-dinitro-1,2,4-triazole system. Since, two sites (N1 and N2) of the 1,2,3-triazole ring are available for N-oxidation (Scheme 12), we fully cbaracterized these salts.

**Scheme 12**. Oxidation of 4,5-dinitro-1,2,3-triazole by OXONE.

The potassium (orange crystals, KODNTz, **15**) and ammonium (yellow crystals, AODNTz, **16**) salts of oxy-4,5,-dinitro-1,2,3-triazole were characterized by X-ray crystallography, DSC, and IR spectroscopy. The X-ray crystal structures of both salts show N-oxidation at the N2 position (Figure 6). The crystal density of the ammonium salt (**16**) is 1.789 g/cc at 20°C, which is similar to the 1,2,4-triazole (AODNT, **6**, ρ = 1.784 g/cc) analogue and bigger than for ammonium 2-oxy-5-nitrotetrazole (AONT, **4**, ρ = 1.703 g/cc).

Figure 6. ORTEP drawing of ammonium 2-oxy-4,5-dinitro-1,2,3-triazole (AODNTz), **16**.
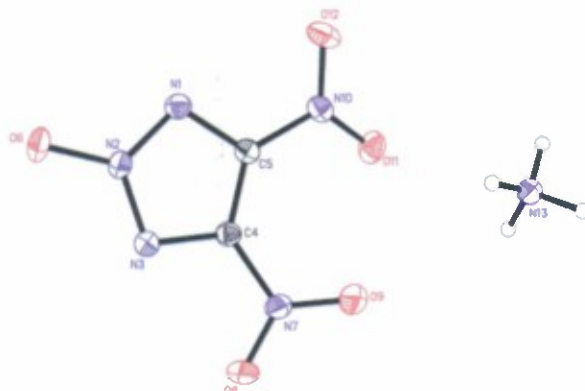
The thermal stability of these salts is high as assessed by preliminary DSC. Preliminary DSC of **16** exhibits a melting point at ~ 190°C with onset to decomposition at ~ 195°C that peaks at ~ 220°C (Figure 7A). This represents a mucb bigher stability than for AONT or AODNT. Minor (< 2%) amounts of red crystals have been found mixed in with some batcbes of the ammonium salt that may be attributed to a less stable N1-bydroxide isomer. The stacked DSC trace in figure 7B shows that thermal stability increases from AODNT, **6** < AONT, **4** << AODNTz, **16**.
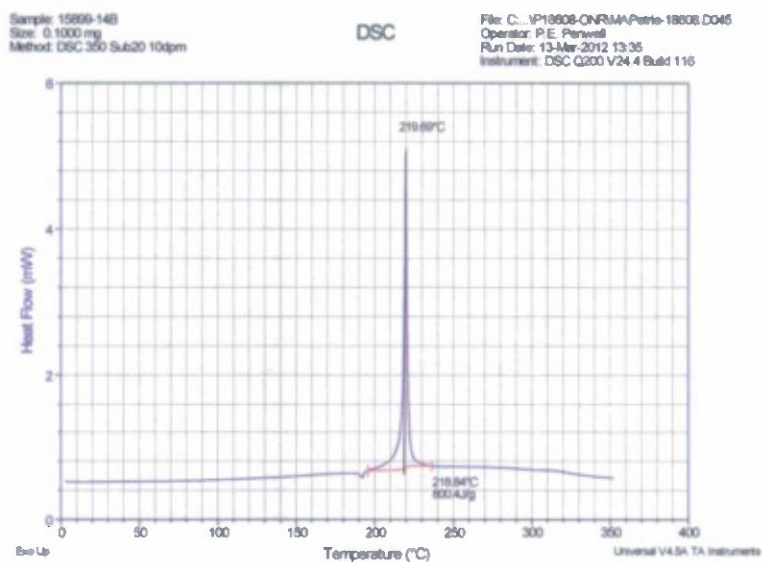
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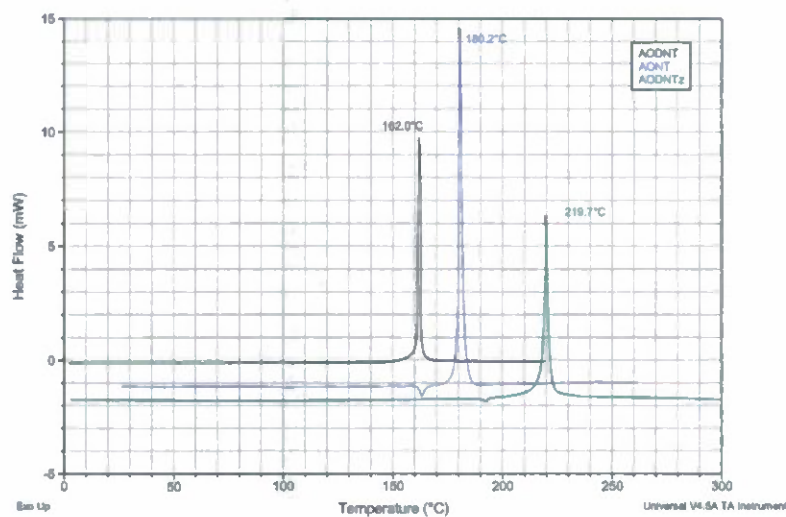
(B)

Figure 7. DSC (A) of ammonium 2-oxy-4,5-dinitro-1,2,3-triazole (AODNTz), **16** and a comparative stacked DSC (B) for AODNT, **6** (black/top), AONT, **4** (blue, middle) and AODNTz, **16** (green/bottom).

Ammonium Oxy-2,4,5-Trinitroimidazole. Ammonium 2,4,5-trinitroimidazole (ATNI) was originally reported in a patent by M. Coburn, (U.S. Patent No. 4028154).[8] This salt has a density of 1.835 g/cc and is stable to 249°C. SRI has attempted to prepare the 1-oxy-2,4,5-trinitroimidazolate and 1,3-dioxy-2,4,5-trinitroimidazolate anions (Figure 8). The ammonium salts of these anions will be over-oxidized by 2 and 3 oxygen atoms, have densities similar to AP, and retain good stability.
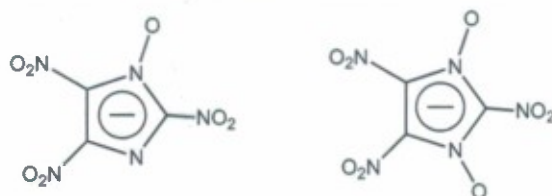
**Figure 8.** 2,4,5-trinitroimidazole oxide and dioxide targets.

Attempts to N-oxidize 2,4,5-trinitroimidazole failed using persulfate or hypofluorous acid. We explored alternate routes to these materials. N1,N3-dioxyimidazole was easily prepared from a known route using glyoxal, formaldehyde, and hydroxylamine (see Scheme 13).[9] From this material, SRI has prepared O-benzyl derivatives of the dioxyimidazole and oxyimidazole. Historically, full nitration of imidazole rings has been problematic due to the unreactive nature of C2 toward acidic nitration; however, Shanthi et al. have reported basic nitration of N-substituted imidazoles at C2 in 60-70% yield.[10] We were unsuccessful in our attempts to nitrate the O-benzyl-protected imidazole rings by deprotonation at C2 and nitration using n-BuONO$_2$ and LiNO$_3$/[CF$_3$C(O)]$_2$O in tetrahydrofuran (THF).
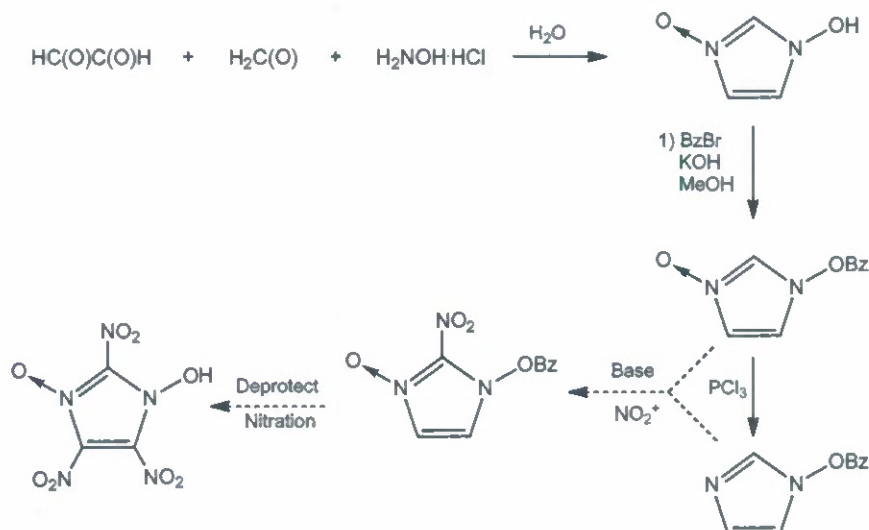
Scheme 13. Proposed route to 2,4,5-trinitroimidazole oxides.

2,2-Dinitropropyl Linkage

SRI is exploring the use of 2,2-dinitropropane as a bridge between highly oxidizing ring structures.[11] This linkage is analogous to the nitraminobismethylene (O$_2$N-N(CH$_2$-)$_2$) linkage used in the construction of 1,1'-(2-nitraza-1,3-propanediyl)-3,5-dinitro-1,2,4-triazole (SRI-100) with a more positive oxygen balance.[12] Linkage of two units of 3,5-dinitro-1,2,4-triazole by 2,2-dinitropropane giving molecule 17 will provide three excess oxygen atoms when balanced to CO and H$_2$O. SRI has explored potential routes to this molecule. The route shown in Scheme 14 gives a high yield of the 2-oximido-1,3-bis-(3,5-dinitro-1,2,4-triazole)propane. We are continuing our attempts to convert this product to the gem-dinitro, 17, by variations of the ponzio reaction.
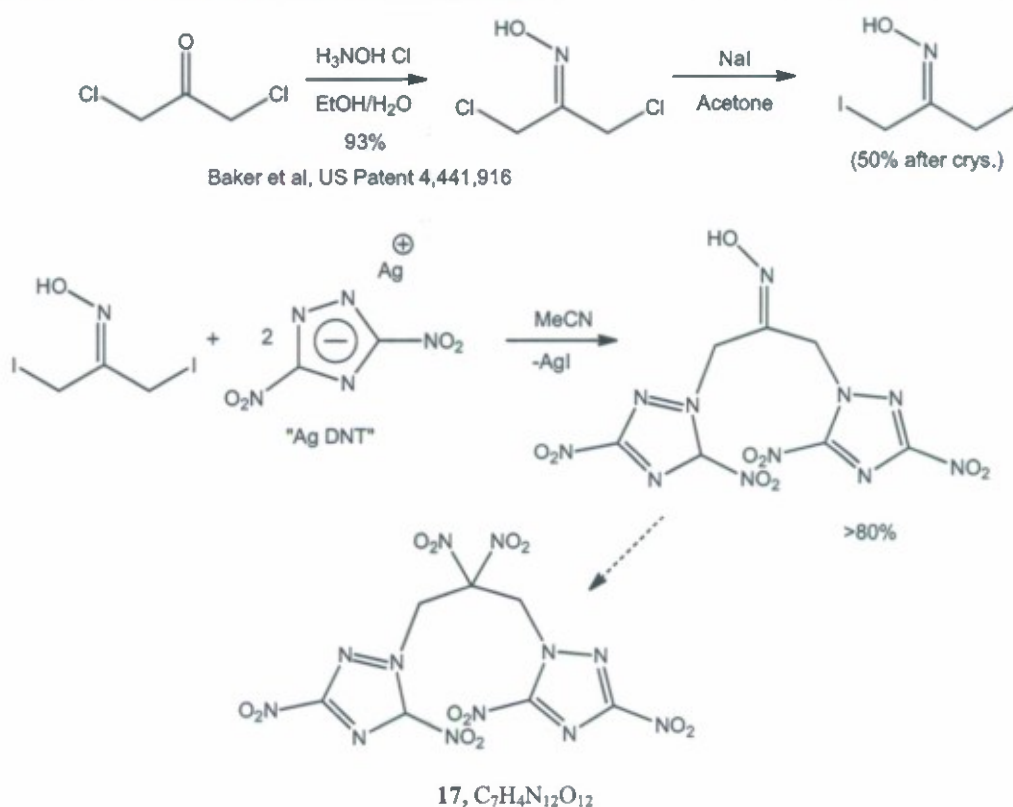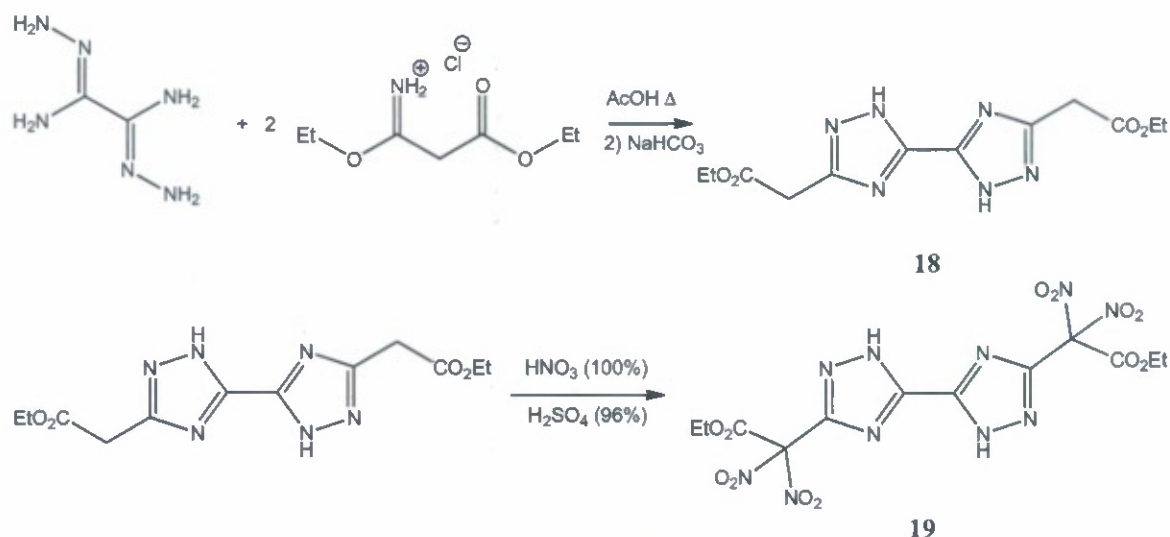
Scheme 14.

Trinitromethyl Substituted Heterocycles

The trinitromethyl group is a highly oxidizing densophore that has found use in a variety of highly oxidized structures, including compounds such as bistrinitroethylnitramine (ρ = 1.960 g/cc) and bistrinitroethylcarbonate (ρ = 1.88 g/cc). SRI is attempting to synthesize examples of trinitromethyl-substituted energetic nitrogenous heterocycle structures. These energetic rings will be highly dense and retain very high oxygen content. We have focused on preparing carbon trinitromethyl (C_{ring}-$C(NO_2)_3$)-substituted rings versus nitrogen trinitromethyl (N_{ring}-$C(NO_2)_3$), considering the former configuration to have higher stability. Our strategy to introduce the -$C(NO_2)_3$ group into heterocyclic structures at carbon has been the nitration of activated methylene groups. Examples of these reactions described in the literature include the nitration of alkanones and acetic-acid-substituted heterocycles.[13] These studies have been limited to C_{ring}-$C(NO_2)_3$-substituted imidazoles, 1,3,5-triazines and N_{ring}-$C(NO_2)_3$-substituted 1,2,4-triazoles. During this program, our group has prepared some examples of energetic and dense C_{ring}-$C(NO_2)_3$-substituted 1,2,4-triazoles and 3,3'-bi-1,2,4-triazoles. Our first target was the 3,3'-bistrinitromethyl-5,5'-bi-*1H*- 1,2,4-triazole, **21** (below) compound. The 3,3'-bi-1,2,4-triazole platform was expected to be more stable and dense than the monocyclic species as previously observed for the nitro-substituted bi-1,2,4-triazole and bi-imidazole compounds.
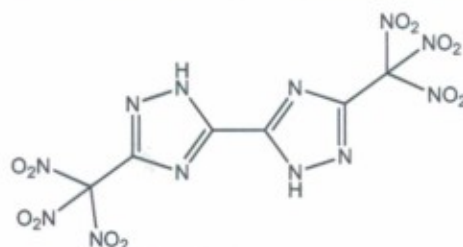
21, $(C_6H_2N_{12}O_{12})$

The 3,3'-bi-*1H*-1,2,4-triazole-5,5'-acetic acid ethyl ester, **18** , precursor to **21**, was prepared by a reported route.[14] Condensation of oxamide dibydrazone (synthesized from dithiooxamide with bydrazine)[15], and ethyl-3-ethoxy-3-iminopropionate hydrochloride in acetic acid gave the diethyl ester, **18**, in 53% yield (Scheme 15). Comparison of m.p., ^{1}H-NMR and IR data to the literature confirm the structure. This material was nitrated in a mixture of 100% HNO_3/96% H_2SO_4 to give the 5,5'-bis(acetic acid-α,α-dinitro)-3,3'-bi-*1H*-1,2,4-triazole diethyl ester, **19**. ^{1}H NMR and IR data are consistent with this structure.

Scheme 15.

Conversion of the acetic acid ethyl ester to the acetic acid bitriazole in Scbeme 16 by the addition of sodium hydroxide followed by acidifying the solution gave a high yield of the acetic acid, **20**. Comparison of ^{1}H-NMR and IR data to the literature confirm the structure.[14] This material was nitrated in 100% HNO_3/96% H_2SO_4 followed by extraction to give ~ 70% yield of 3,3'-bistrinitromethyl-5,5'-bi-*1H*-1,2,4-triazole, **21** and was cbaracterized by DSC, X-ray crystallography, ^{1}H and ^{13}C NMR, and IR. Compound **21** is relatively stable with an onset to decomposition of ~ 133°C.

20

Scheme 16.
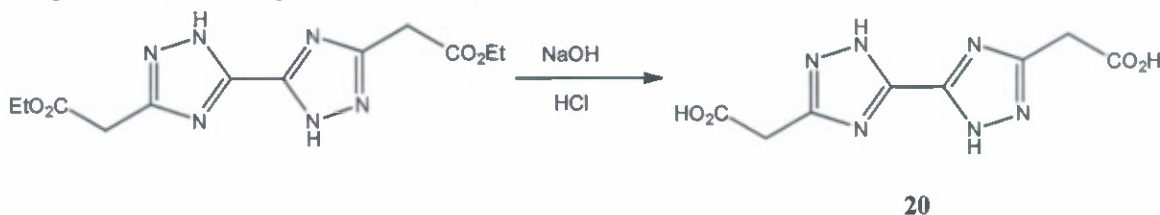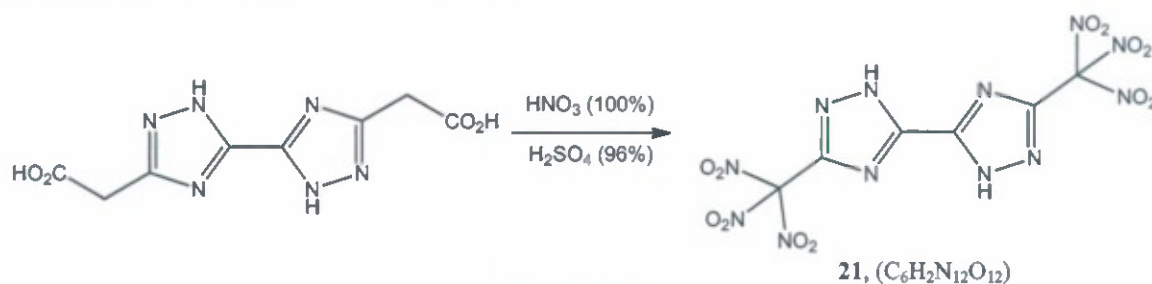
Crystals used for the X-ray analysis of **21** were grown from diethyl ether and contained ether molecules for every bitriazole (Figure 9). Unfortunately, attempts to grow crystals from other solvents have not produced X-ray quality crystals of the non-solvated form.

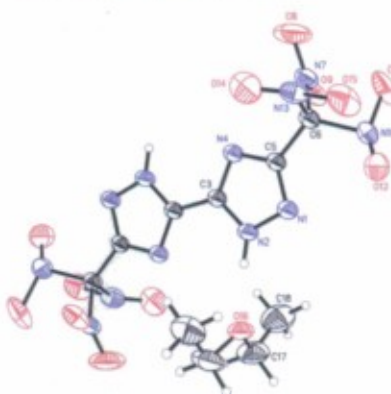**Figure** 9. A view of the molecular structure of **21** showing the inclusion of ethyl ether solvent.

The trinitromethyl-substituted monocyclic 5-nitro-3-trinitromethyl-*1H*-1,2,4-triazole, **22**, was synthesized by an analogous route shown in Scheme 17. The precursor 5-amino-*1H*-1,2,4-triazole-3-yl-acetic acid was prepared by a published procedure of refluxing aqueous aminoguanidine bicarbonate and malonic acid.[16]
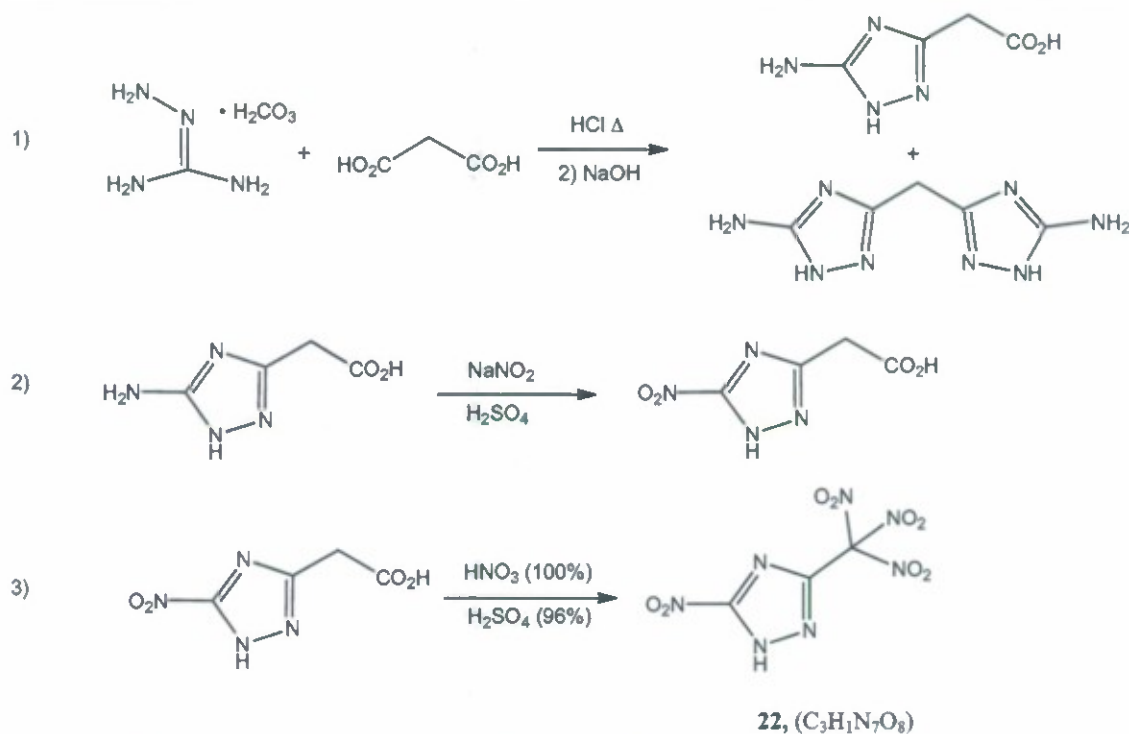
Scheme 17. Synthesis route to 5-nitro-3-trinitromethyl-*1H*-1,2,4-triazole, **22**.

This material was subjected to diazotization conditions (2) using excess nitrite ion to generate 5-nitro-*1H*-1,2,4-triazole-3-yl-acetic acid.[17] Attempts to oxidize the amino to nitro using hydrogen peroxide and sodium tungstate were unsuccessful. The nitration of 5-nitro-*1H*-1,2,4-triazole-3-yl-acetic acid using 100% HNO_3/96% H_2SO_4 gave a good (73%) yield of 5-nitro-3-trinitromethyl-*1H*-1,2,4-triazole, **22**, after work-up. Compound **22** was characterized by DSC, X-ray crystallography, ^{1}H NMR, and IR. The crystalline density of **22** was 1.950 g/cc at 20°C by X-ray. The nitro groups of the trinitromethyl are virtually perpendicular to each other. The ring nitro group is 9.9° out of the triazole plane (Figure 10). The DSC of **22** shows a melt at 112.6°C followed immediately by a strong exothermic decomposition. The density (ρ = 1.901 g/cc at 20°C) and thermal stability of the N_{ring}-C(NO_2)_3$, 3-nitro-1-trinitromethyl-5H-1,2,4-triazole analog are slightly less than that for compound **22**.
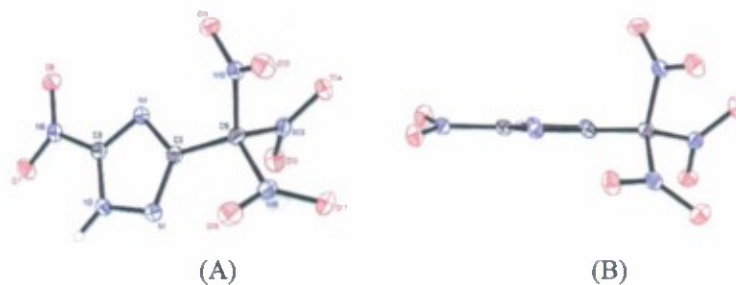

Figure 10. Overhead (A) and side (B) ORTEP views of 5-nitro-3-trinitromethyl-*1H*-1,2,4-triazole, **22**.

More recently, SRI has undertaken the synthesis of the 3-trinitromethyl analog to the well-known explosive 3-nitro-1,2,4-triazol-5-one (NTO) (see below). The properties of NTO are very attractive; it has a high density, high thermal and chemical stability, and is insensitive. We hoped these attributes would be shared by the 3-trinitromethyl or 3-dinitromethylene derivatives. The urea and trinitromethyl frameworks should impart very high density, while the thermal and chemical stability of this compound are more unpredictable.

NTO   **23**, $(C_3H_2N_6O_7)$
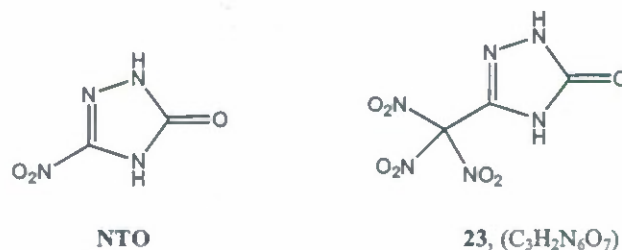
The synthesis of **23** was attempted using a three-step procedure from readily available starting materials (Scheme 18). Following a published preparation, the first step involves reaction (1) between diethyl malonate and acetone semicarbazone in solution with sodium ethoxide to give 1-isopropylideneaminobarbituric acid sodium salt. On adjustment to pH ~ 6, the Schiff base is converted to the sodium salt of 1-barbituric acid in ~ 84% yield (see below).[18] The acid catalyzed isomerization (2) of 1-barbituric acid gave 3-acetic acid-1,2,4-triazol-5-one in ~ 70% yield.[19] The melting point and ^1H NMR shifts of synthesized 3-acetic acid-1,2,4-triazol-5-one were consistent with values reported in the literature. Nitration of 3-acetic acid-1,2,4-triazol-5-one was achieved using 100% HNO_3/96% H_2SO_4 to give **23**.
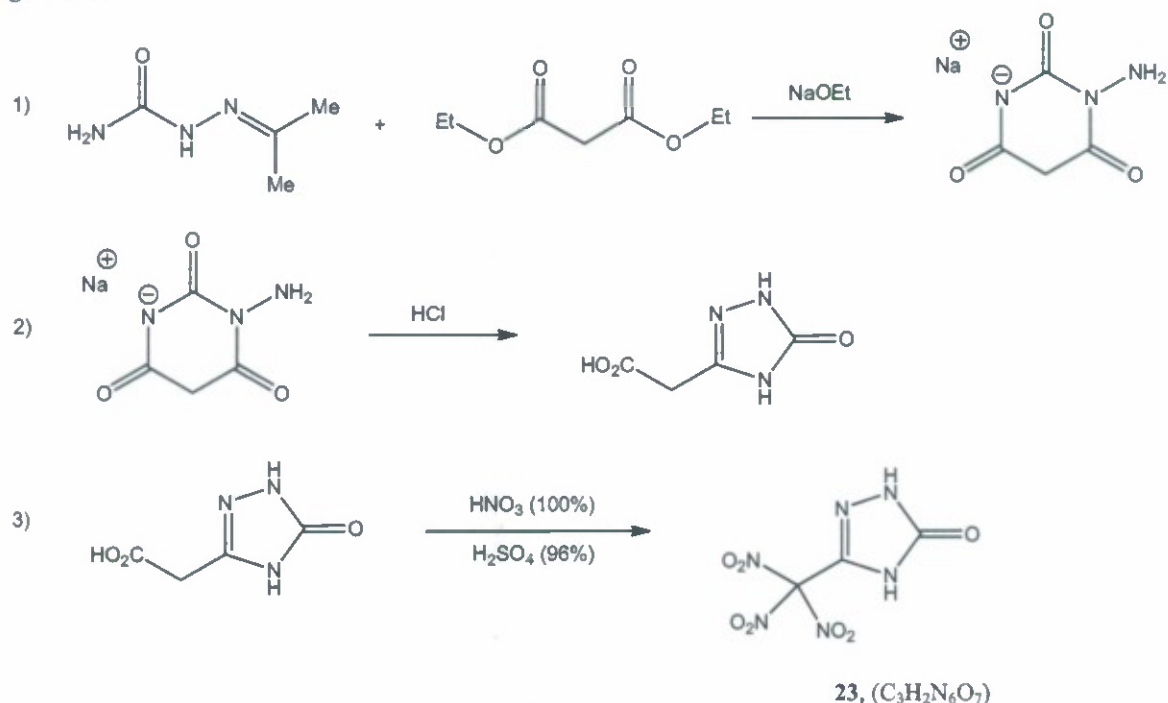
Scheme 18. Synthesis of 3-trinitromethyl-1,2,4-triazol-5-one, **23**.

The DSC spectrum of **23** shows a very low onset to decomposition of 70°C. Structural assignment is, in part, supported by the absence of methylene resonances in the ^{1}H NMR spectrum and infrared stretches in the vicinity (1630-1595 cm^{-1}) of those expected for the trinitromethyl functional group and a urea carbonyl stretch of 1715 cm^{-1}. The growth of X-ray-quality crystals of product **23** in a variety of solvents was difficult due to thermal and chemical instability. Suitable crystals for X-ray analysis were eventually grown from nitromethane. The structure was verified and density ($\rho = 1.885$ g/cc at 150K) calculated by X-ray (Figure 11). This density is similar to that of NTO ($\rho = 1.878$ g/cc (β-form) and $\rho = 1.92$ g/cc (α-form). The salts of **23** should enhance thermal stability.
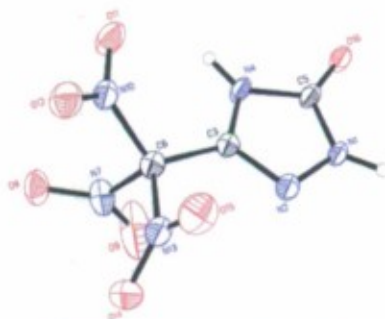
Figure 11. ORTEP drawing for the structure of 3-trinitromethyl-1,2,4-triazol-5-one, **23**.

The synthesis of the 3-acetic acid-1,2,4-triazol-5-one ethyl ester was easily achieved by refluxing 3-acetic acid-1,2,4-triazol-5-one in ethanol saturated with hydrogen chloride (Scheme 19). Nitration of this material using 100% HNO$_3$/96% H$_2$SO$_4$ gave a compound whose characterization by ^{1}H NMR, IR, and DSC is consistent with the 3-acetic acid-α,α-dinitro-1,2,4-triazole-5-one ethyl ester structure, **24**. The onset to decomposition observed for **24** in the DSC is higher (+20°C) at 89°C than for the 3-trinitromethyl analogue, **23** ($\sim$70°C) with a very similar two-peak decomposition profile (Figure 12).
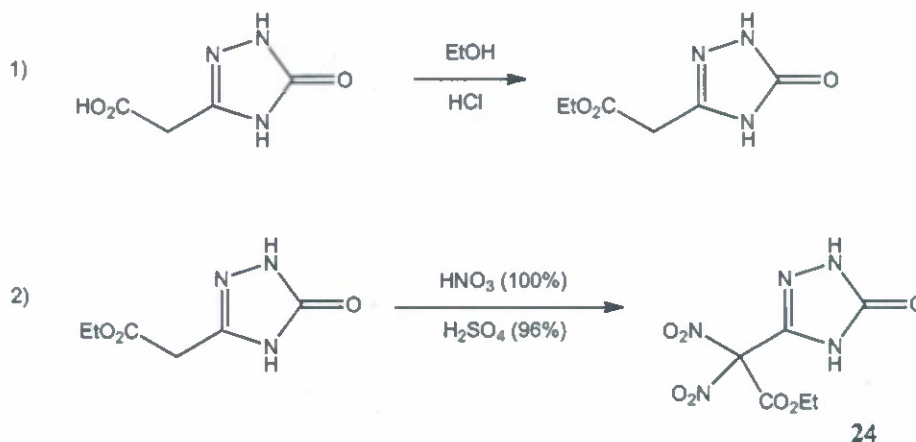
Scheme 19. Synthesis of 3-acetic acid-α,α-dinitro-1,2,4-triazole-5-one ethyl ester, **24**.
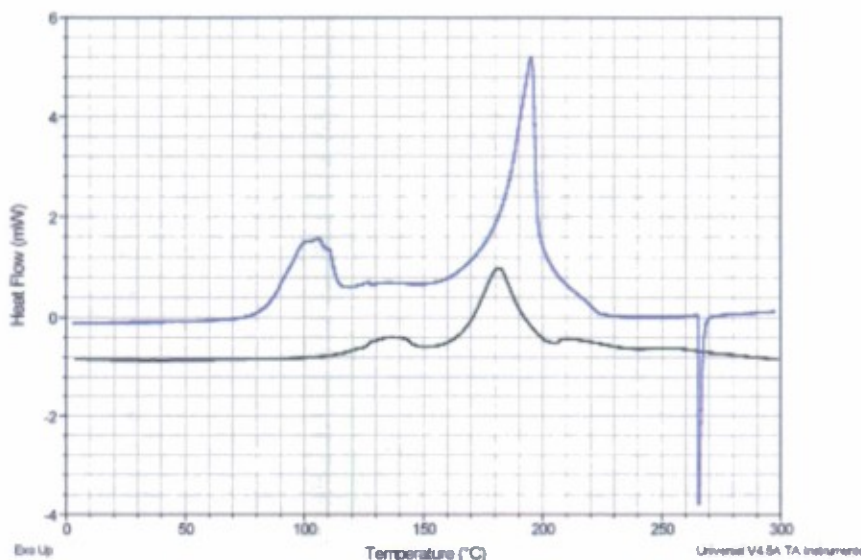
Figure 12. Comparative DSC of **23** (top/blue) and **24** (bottom/black).

Conclusions and Prospective Future Research

SRI has made progress in several areas of interest to the Navy work thrusts, specifically in the areas of AP replacement and insensitive RDX/HMX replacements. Our ongoing research has advanced the field of energetic materials, providing new synthesis methodologies, new targets for future basic research and synthesized compounds that can be prepared for further testing by the Navy. N_{ring}-oxidation of nitroheterocycles can boost oxygen content and increase density of the parent material. The oxidation of 5-nitrotetrazole by OXONE and conversion to the ammonium salt (AONT) has been optimized for safe and reliable larger-scale synthesis. Synthesis methodology for more difficult ring N-oxidation of nitroheterocycles has been expanded to include the use of hypofluorous acid (HOF), which includes the synthesis of the oxidizing anion, 1-oxy-3,5-dinitro-1,2,4-triazole (ODNT). The ammonium (AODNT) and potassium (KODNT) salts were prepared and characterized. The N2-oxidation of 4,5-dinitro-1,2,3-triazole by OXONE has demonstrated. The thermal stability and density of the ammonium 2-oxy-4,5-dinitro-1,2,3-triazole (AODNTz) is very attractive. SRI recommends that the ammonium salts of ONT, ODNT and ODNTz be further evaluated for use as AP replacements, with emphasis as minimum-smoke propellant ingredients in combination with ammonium nitrate. Preliminary Cheetah performance calculations have shown these formulations can outperform the baseline AP/Al/HTPB propellants. Calculations have also shown that these materials may have value as RDX/HMX replacements. A vast area of research on N-oxidized nitroheterocycles is awaiting exploration using these powerful methods of N-oxidation.

The synthesis of 1,1'-diamino-4,4',5,5'-tetranitro-2,2'-biimidazole (DATNBI) was required as an intermediate to the proposed final azo-linked target, **1**. DATNBI is prepared in three steps and has excellent thermal properties and density. DATNBI is stable to 200°C with a high crystal density of 1.934 g/cc at 21° and calculated heat of formation of 97.3 kcal/mole. Theoretically, DATNBI outperforms RDX and comes close to HMX with a detonation pressure of 367.3 kbar and detonation velocity of 9.002 km/s. Efforts to synthesize other examples of high density N-amino or N-oxides of bi-heterocycle rings systems should yield very interesting candidates for insensitive RDX/HMX replacements.

The trinitromethyl functional group greatly enhances density and contributes large amounts of oxygen. There are relatively few examples of trinitromethyl-substituted heterocycles. SRI and others have demonstrated that nitration of carbon-substituted acetic acid heterocycles gives good yields of the trinitromethyl derivatives. These derivatives exhibit very high density and high oxygen balance. The downside is that they also exhibit lower thermal stability and enhanced shock sensitivity. So far, of the 1,2,4-triazole derivatives prepared by SRI and others, compound 21, 3,3'-bistrinitromethyl-5,5'-bi-*1H*-1,2,4-triazole, shows the highest thermal stability with an onset to decomposition of ~ 133°C.

Experimental Section

1,1'-Diamino-4,4',5,5'-tetranitro-2,2'-biimidazole (DATNBI), 3:   4,4',5,5'-tetranitro-2,2'-bi-*1H*-imidazole was previously prepared by the methods of Cbo et al.[1] 4,4',5,5'-tetranitro-2,2'-bi-*1H*-imidazole (2.03 g, 6.5 mmol) was combined with two equivalents of DBU in acetonitrile (75 mL) to give the bis DBU salt of 4,4',5,5'-tetranitro-2,2'-bi-*1H*-imidazole. The orange solid was isolated by filtration and drying in air. Excess of two equivalents of hydroxylamine-O-toluene sulfonate (1.02g, 5.45 mmol) previously prepared in chloroform solution (~ 30 mL) was added to the bis DBU salt of 4,4',5,5'-tetranitro-2,2'-bi-*1H*-imidazole (0.84g, 1.36 mmol) in acetonitrile (~ 20 mL) and stirred ~16 h. Volatiles were removed and the residue dissolved in a minimum of ethyl acetate, washed with water and dried over $MgSO_4$. Purification by flash column chromatograpby gave a yellow solid (270 mg, 65%). T_{melt} 205°C with immediate post melt decomposition, IR (KBr): 3362, 3261, 1595, 1533, 1389, 1366, 1325, 1147, 1041, 851, 817, 760, 748, 709, 643 cm^{-1}. ^1H NMR (d_6-dmso): δ 6.97. $^{13}C\{^1H\}$ NMR: δ 135.4, 134.0, 131.4 ppm.

Ammonium 1-oxy-3,5-dinitro-1,2,4-triazole (AODNT), 6: Potassium 3,5-dinitro-1,2,4-triazole was prepared from 3,5-diamino-1,2,4-triazole using reported methods.[20] Solid potassium 3,5-dinitro-1,2,4-triazole (0.50 g, 2.54 mmol) was added to a previously prepared HOF solution (88 mL, ~ 0.25M) acetonitrile/water (80 mL/10 mL) solution at -5°C and stirred ~ 1 b. The solid dissolved giving a bright yellow-colored solution with evolved gases. After neutralizing with potassium bicarbonate, all volatiles were removed, the solids extracted with acetonitrile, and solution was filtered. Removal of solvent gave solids that were recrystallized to give orange crystals. Yield was ~ 0.30 g, 55%, and purity was 96.7% by capillary ion chromatography analysis. The ammonium salt was prepared using the tributylammonium salt in the presence of ammonia. Ion analysis of yellow crystals of the ammonium salt shows ~ 100% N-oxide. Potassium salt, 5: crystal density (X-ray) of 2.088 g/cc at ~20°C. DSC: melt at ~ 212°C with immediate onset to decomposition. IR (KBr): 1565, 1539, 1501, 1406, 1319, 1240, 1099, 1023, 874, 823, 764, 639 cm^{-1}. $^{13}C\{^1H\}$ NMR (d_6-dmso): δ 147.3, 143.0 ppm. Ammonium salt, 6: crystal density (X-ray) of 1.784 g/cc at ~20°C and an estimated ΔH_f = +25 kcal/mole. DSC: sharp onset to decomposition ~ 145°C without melting. IR (KBr): 3318, 3164, 2923, 2852, 1564, 1545, 1501, 1403, 1332, 1234, 1105, 1025, 872, 823, 762, 640 cm^{-1}.

N-Benzylideneaminoacetonitrile, 7: A total of 9.76 mL (70.0 mmol) of triethylamine followed by 3.56 mL (35.0 mmol) of benzaldebyde was added to a mixture of 5.40 g (35.0 mmol) of aminoacetonitrile monosulfate in 55 mL of CH_2Cl_2 under argon. The mixture was heated in a 65°C oil bath for 2 hrs using a Dean-Stark trap to separate the water azeotrope. The mixture was cooled, washed with water and brine, dried (K_2CO_3), filtered and concentrated to 4,78 g (95%) of 7 as an oil: ^1H NMR ($CDCl_3$) 4.65 (d, J = 1.8 Hz, 2H), 7.40-7.55 (m, 3H), 7.78 (dd, J = 1.6, 7.5 Hz, 2H), 8.52 (t, J = 1.6 Hz, 1H) ppm.

p-Methoxybenzyl azide, 8: To a mixture of 2.93 g (45.0 mmol) of sodium azide in 20 mL of DMF was added 4.09 g (30.0 mmol) of *p*-methoxybenzyl chloride under argon at 0°C. The mixture was allowed to warm to room temperature and was stirred overnight. The mixture was poured into water and extracted with hexanes. The organic extracts were washed with water and brine, dried (MgSO4), filtered and concentrated to 4.84 g of an oil. Flash column chromatography (hexanes/CH_2Cl_2, 1:1) through silica gave

8 (4.81 g, 98%) as a colorless oil: ^{1}H NMR (CDCl$_3$) 3.75 (s. 3H), 4.20 (s, 2H), 6.84 (d, J = 8.4 Hz, 2H), 7.18 (d, J = 8.4 Hz, 2H) ppm.

5-Amino-4-(N-benzylidene)-1-(p-methoxybenzyl)-1,2,3-triazole, 9: A total of 14.1 mL (35.3 mmol) of a 2.5M solution of n-butyllithium in hexanes was added over 10 min. to a -30°C cooled mixture of 5.46 (38.9 mmol) of diisopropylamine in 45 mL of THF with stirring under argon. The mixture stirred for 20 min longer in an ice-water bath and then cooled to -78°C. A mixture of 5.10 g (35.3 mmol) of N-benzylideneaminoacetonitrile **7** in 10 mL of THF was added over 10 min. After 2 min. longer, 4.79 g (29.35 mmol) of p-methoxybenzyl azide **8** in 10 mL of THF was added over 10 min. to the red mixture. The mixture was stirred at -78°C for 2 hrs and allowed to warm to room temperature over 3 hrs and stirred overnight. The mixture was poured into ice-water containing 4.83g (35.0 mmol) of Na$_2$HPO$_4$ and extracted with 9:1 ethyl acetate/hexanes. The organic extracts were washed with water and brine, dried (K$_2$CO$_3$), filtered, and concentrated to 10.2 g of the crude product mixture. Purification by flash column chromatography (CH$_2$Cl$_2$/EtOAc, 5:1) gave 4.96 g (55%) of 9, which was crystallized from Et$_2$O to afford 4.18 g (47%) of 9 as a colorless powder: ^{1}H NMR (CDCl$_3$) 3.77 (br s, 2H), 3.80 (s, 3H), 5.37 (s, 2H), 6.90 (d, J = 7.5 Hz, 2H), 7.21 (d, J =7.5 Hz, 2H), 7.38-7.45 (m, 3H), 7.82-7.90 (m, 2H), 9.19 (s, 1H) ppm. IR (KBr): 3441, 3289, 3174, 2960, 2928, 1632, 1582, 1513, 1289, 1252, 1217, 1177, 1114, 1037, 776, 756, 691 cm^{-1}.

4,5-Diamino-1-(p-methoxybenzyl)-1,2,3-triazole, 10: A total of 1.02g (14.6 mmol) of hydroxylamine hydrochloride was added with stirring to 4.09 g (13.30 mmol) of 5-amino-4-(N-benzylidene)-1-(p-methoxybenzyl)-1,2,3-triazole 9 in 56 mL of THF and 28 mL of water in a 15°C water bath. After 30 min., 2.76g (20.0 mmol) of potassium carbonate was added and the mixture was stirred for 10 min. and concentrated to a solid. The residue was taken up in EtOAc and purified by flash column chromatography. The product **10** was eluted with EtOAc/MeOH (4:1) to give 2.77 g of a solid, and Et$_2$O was added. After filtration and drying under vacuum, 2.52 g (87%) of the product **10** was obtained as a nearly colorless powder: ^{1}H NMR (acetone-d$_6$) 3.04 (br s, 2H), 3.07 (br s, 2H), 3.78 (s, 3H), 5.28 (s, 2H), 6.86 (d, J = 9.0 Hz, 2H), 7.18 (d, J = 9.0 Hz, 2H) ppm. IR (KBr): 3357, 3290, 3157, 2958, 2923, 2834, 1632, 1515, 1440, 1379, 1250, 1207, 1118, 1037, 890, 830, 802 cm^{-1}.

5-Amino-1-(p-methoxybenzyl)-4-nitro-1,2,3-triazole, 11: A 10% F$_2$/90% N$_2$ gas mixture was bubbled into a -15°C cooled mixture of 70 mL of acetonitrile and 7 mL of water for 30 min. to give a hypofluorous acid-acetonitrile complex, which was cooled to -26°C. In a separate round bottom flask, a -26°C cooled mixture of 220 mg of 4,5-diamino-1-(p-methoxybenzyl)-1,2,3-triazole **10** was stirred in 10 mL of acetonitrile. The cold hypofluorous acid-acetonitrile mixture was added all at once to the mixture of **10** in acetonitrile. The mixture immediately became blue in color. After 2 seconds, the reaction had become yellow in color and was immediately quenched with 50 mL of saturated aqueous sodium bicarbonate. The mixture was extracted with ethyl acetate and concentrated. The residual solid was taken up in dichloromethane, dried (K$_2$CO$_3$), filtered, and concentrated to 211 mg of a solid. Purification by flash column chromatography (CH$_2$Cl$_2$/EtOAc, 9:1) afforded 180 mg (72%) of **11** as a light yellow solid: ^{1}H NMR (CDCl$_3$) 3.82 (s, 3H), 5.28 (br s, 2H), 5,40 (s, 2H), 6.95 (d, J = 9.0 Hz, 2H), 7.22 (d, J = 9.0 Hz, 2H) ppm. IR (KBr): 3452, 3276, 3210, 3146, 2923, 2852, 1639, 1512, 1492, 1467, 1438, 1398, 1246, 1182, 1117, 1069, 1026, 842, 787 cm^{-1}.

4,5-Dinitro-1-(p-methoxybenzyl)-1,2,3-triazole, 12: A 10% F$_2$/90% N$_2$ gas mixture was bubbled into a −15°C cooled mixture of 80 mL of acetonitrile and 8 mL of water for 30 min. to give a hypofluorous acid-acetonitrile complex. In a separate round bottom flask, a -15°C cooled mixture of 166 mg (0.76 mmol) of 4,5-diamino-1-(p-methoxybenzyl)-1,2,3-triazole in 8 mL of acetonitrile was stirred. The cold hypofluorous acid-acetonitrile mixture was added all at once to the mixture of **10** in acetonitrile. The mixture immediately became blue in color and quickly turned yellow. After 3 minutes of stirring at −15°C, the mixture was quenched with 50 mL of saturated aqueous sodium bicarbonate. The mixture was extracted with dichloromethane, washed with water and brine, dried (K$_2$CO$_3$), filtered, and concentrated

to 143 mg of the product mixture. Purification by flash column chromatography (hexanes/CH_2Cl_2, 1:1) afforded 36 mg (17%) of **12** as a yellow crystalline solid: ^{1}H NMR ($CDCl_3$) 3.80 (s, 3H), 5.78 (s, 2H), 6.90 (d, J = 9.0 Hz, 2H), 7.27 (d, J = 9.0 Hz, 2H) ppm. Continued elution with CH_2Cl_2/EtOAc (9:1) afforded 83 mg (44%) of **7**. IR (KBr): 3435, 3017, 2964, 2920, 2849, 1615, 1575, 1545, 1516, 1455, 1376, 1353, 1306, 1254, 1178, 1032, 849, 817 cm^{-1}.

5-Amino-4-nitro-1,2,3-triazole, 13: A mixture of 175 mg (0.70 mmol) of 5-amino-1-(*p*-methoxybenzyl)-4-nitro-1,2,3-triazole and 0.36 mL (3.30 mmol) of anisole in 6 mL of trifluoroacetic acid was heated to reflux in a 90°C oil bath for 36 hrs with stirring under argon. The mixture was concentrated, and Et_2O was added. Upon warming, a colorless solid separated, and the solid was filtered, washed with Et_2O, and dried to afford 76 mg (85%) of **13**: ^{1}H NMR (DMSO-d_6) 3.31 (br s, 2H), 7.42 (br s, 1H) ppm. IR (KBr): 3372, 3241, 3172, 1652, 1474, 1454, 1352, 1295, 1257, 1213, 1123, 1053, 1011, 974, 762, 669, 577 cm^{-1}. NMR shifts and IR stretches are similar to those found in the literature.[7]

4,5-Dinitro-1,2,3-triazole, 14 potassium salt: A mixture of 107 mg (0.38 mmol) of 4,5-dinitro-1-(*p*-methoxybenzyl)-1,2,3-triazole 9 and 0.16 mL (1.8 mmol) of anisole in 4.0 mL of trifluoroacetic acid and 1.5 mL of dichloromethane was heated at reflux in a 60°C oil bath under argon for 1 day. The mixture was concentrated, and 50 mg (0.50 mmol) of aqueous potassium bicarbonate was added. The aqueous mixture was filtered through glass wool, concentrated, taken up in acetonitrile, and again filtered through glass wool and concentrated to afford 74 mg (99%) of **14** as a yellow solid. IR (KBr): 1518, 1393, 1376, 1302, 1167, 1132, 857, 815, 754 cm^{-1}.

4,5-Dinitro-1,2,3-triazole, potassium salt (14, Baryshnikov route)[7]: A mixture of 7.8 mL H_2O_2 and 15 mL of H_2SO_4 was prepared at 0°C. To this mixture, 1.0 g (7.75 mmol) of 4-amino-5-nitro-1,2,3-triazole was slowly added over ~ 20 min., keeping the temperature within the range 0-15°C. This mixture was allowed to set in the refrigerator at 7-8°C for 24 hrs. The mixture was then added to 100 mL cold (0°C) water. The mixture was extracted with 3 x 50 mL of Et_2O, dried over $MgSO_4$, and concentrated to give 4,5-dinitro-1,2,3-triazole as a light yellow oil. The oil was dissolved in 20 mL of MeOH, and solid $KHCO_3$ was slowly added until pH neutral. After filtration and removal of all volatiles, 30 mL of Et_2O was added to precipitate 0.52 g (34%) of potassium 4,5-dinitro-1,2,3-triazole as a yellow solid. The IR spectrum of this material is identical to that of **14**.

2-Oxy-4,5-dinitro-1,2,3-triazole, potassium salt (KODNTz), 15: Solid potassium 4,5-dinitro-1,2,3-triazole (100 mg, 0.51 mmol) was added to a mixture of 0.78 g (1.26 mmol oxidant) of OXONE and 0.22 g (1.26 mmol) of K_2HPO_4 in 7 mL of water. This mixture was heated at 55°C for ~ 20 hrs while stirring. Additional K_2HPO_4 was added in 1 mL of water to adjust to pH ~ 6, and the heating continued for an additional 24 hrs. The yellow mixture was cooled to room temperature and acidified using 20% H_2SO_4. The mixture was extracted with 3 x 20 mL of Et_2O. The ether fractions were dried over MgSO4, filtered, and volatiles removed to give a small amount of yellow oil. The oil was dissolved in 10 mL of MeOH, and solid $KHCO_3$ (~ 50 mg) was slowly added until pH neutral. After filtration and removal of all volatiles, the solid was dissolved in 2 mL of MeOH, and 30 mL of Et_2O was added to precipitate ~ 75 mg (65%) of an orange solid. Solid **15** was recrystallized from minimal EtOH. Crystal density (X-ray) of 2.081 g/cc at ~ 20°C. IR (KBr): 1566, 1539, 1501, 1406, 1319, 1240, 1099, 1023, 874, 823, 764, 639 cm^{-1}.

2-Oxy-4,5-dinitro-1,2,3-triazole, ammonium salt (AODNTz), 16: Solid potassium 4,5-dinitro-1,2,3-dinitro-1,2,3-triazole (185 mg, 0.93 mmol) was added to mixture of 1.43 g (2.32 mmol oxidant) of OXONE and 0.40 g (2.30 mmol) of K_2HPO_4 in 10 mL of water. This mixture was heated at 55°C for ~ 20 hrs while stirring. Additional K_2HPO_4 was added in 1 mL of water to adjust to pH ~6, and the heating continued for an additional 24 hrs. The yellow mixture was cooled to room temperature and acidified using 20% H_2SO_4. The mixture was extracted with 3 x 20 mL of Et_2O. The ether fractions were dried over MgSO4, filtered, and volatiles removed to give a small amount of yellow oil. The oil was

dissolved in 10 mL of Et_2O, and ammonia (NH_3) saturated Et_2O solution added until pH neutral. The yellow crystals of **16** were isolated by filtration, rinsed with Et_2O and air dried to give ~68 mg (41%) of product. Crystal density (X-ray) of 1.789 g/cc at ~20°C. IR (KBr): 3307, 3177, 2962, 1516, 1421, 1405, 1352, 1304, 1172, 1131, 815, 782, 678 cm^{-1}.

3,3'-Bistrinitromethyl-5,5'-bi-1H-1,2,4-triazole, 21: Solid 3,3-Bis(1,2,4-triazole)-5,5'-diacetic acid dihydrate (0.30 g, 1.04 mmol) was added to a mixture of 100% nitric acid (1.20 mL) and 96% sulfuric acid (3.8 mL) and cooled to 0°C. The mixture was stirred ~ 17 h at ~ 23°C and slowly poured into ice cold water (10 mL), keeping the temperature < 10°C. The solid product was filtered, rinsed with cold water, and allowed to air dry. Yield ~ 0.32 g, ~ 70%. Onset to decomposition ~ 133°C without melting. IR (KBr): 3257, 1636, 1595, 1499, 1438, 1407, 1336, 1285, 1200, 1177, 1073, 992, 959, 844, 799, 755, 671, 638 cm^{-1}. $^{13}C\{^1H\}$ NMR : δ 150.4, 147.4, 123.6 ppm.

5-Nitro-3-trinitromethyl-1H-1,2,4-triazole, 22: Solid 5-nitro-1H-1,2,4-triazole-3-yl-acetic acid hydrate (0.53 g, 2.79 mmol) was added to a mixture of 100% nitric acid (2.0 mL) and 96% sulfuric acid (6.6 mL) cooled to 0°C. The reaction mixture was stirred for ~ 17 h at ~ 23°C and slowly poured into water (20 mL) at 0°C keeping the temperature at < 10°C. The mixture was extracted with ethyl acetate (3 x 25 mL), and the organic layer was separated, washed with water, and dried over Na_2SO_4. The oil was dissolved in warm methylene chloride, which gave crystals after cooling to 0°C. Yield 0.62 g, 73%. T_{melt} 112.7°C with immediate post melt decomposition. IR (KBr): 3132, 1612, 1573, 1523, 1481, 1371, 1281, 1175, 1080, 1044, 963, 846, 829, 801, 633 cm^{-1}.

3-Trinitromethyl-1,2,4-triazol-5-one, 23: Solid 3-acetic acid-1,2,4-triazol-5-one (0.50 g, 3.50 mmol) was added to a mixture of 100% nitric acid (2.0 mL) and 96% sulfuric acid (6.6 mL) cooled to 0°C. The reaction mixture was stirred for ~ 17 h at ~ 23°C and slowly poured into water (20 mL) at 0°C, keeping the temperature at < 10°C. The mixture was extracted with ethyl acetate (3x50 mL), and the organic layer was separated, washed with 25 mL of water, and dried over $MgSO_4$. Removal of all volatiles gave a crude yield of 0.28 g, 35%. X-ray quality crystals were grown from nitromethane. T_{onset} ~ 70°C. IR (KBr): 3188, 3052, 2923, 1716, 1633, 1596, 1475, 1354, 1283, 11070, 1038, 945, 842, 800, 779, 747, 610, 565 cm^{-1}.

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